

Copolymers of Vinyl Alcohol and Vinyl Stearate*

EDMUND F. JORDAN, JR., WILLIAM E. PALM, DANIEL SWERN,
LEE P. WITNAUER, and WILLIAM S. PORT, *Eastern Regional
Research Laboratory, † Philadelphia 18, Pennsylvania*

The use of poly(vinyl alcohol) has been restricted, in large measure, because of its sensitivity to water. Its solubility prevents its use as a fiber although the oriented polymer has a high tensile strength.^{1,2} Much work has been done, especially in Japan, to produce water insolubility by treating the fiber as it is formed with an aldehyde.¹⁻³ Chemical treatment with dimethylol urea, trimethylol melamine, chromium and titanium compounds, and other reagents³ has been used.

Another method of achieving insolubility is the preparation of a copolymer of vinyl alcohol and a monomer which is water repellent such as, for example, a fatty monomer. Because poly(vinyl alcohol) is usually prepared by hydrolysis of a poly(vinyl ester), a practical synthesis of a copolymer of vinyl alcohol would require the selection of a monomer which copolymerizes readily with a vinyl ester. Also, it is necessary that the copolymer segment formed from this comonomer hydrolyze at a much slower rate than that for the vinyl ester selected. Both requirements are met by vinyl formate as the vinyl ester and vinyl stearate as the comonomer. Previous work⁴ has already shown that the length of the acyl chain in vinyl esters does not materially alter the monomer reactivity ratios. It may be expected, therefore, that compositionally homogeneous copolymers of vinyl formate and vinyl stearate can be prepared from any proportions of the two monomers. Because it is known that poly(vinyl formate) hydrolyzes at a higher rate⁵ than do other poly(vinyl esters), it was reasoned *a priori*, that in the copolymers a differential rate would also be found.

Certain problems requiring solution were recognized from the beginning. Because vinyl formate hydrolyzes rapidly in water, neither suspension nor emulsion polymerization procedures can be used. Mass polymerization in the presence of a low concentration of a solvent having a low chain transfer constant was therefore indicated.⁶ The effects of the conditions of polymerization (temperature, the type and the concentration of solvent, and the initiator concentration) on the intrinsic viscosity of the poly(vinyl

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† A Laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

formates) formed were also to be studied because mechanical properties of polymers are known to be related to their molecular weight and their linearity. Investigations on methods of hydrolysis of copolymers of vinyl formate and vinyl stearate were required. Finally, a study relating mechanical properties and composition of copolymers of vinyl alcohol and vinyl stearate was to be undertaken.

EXPERIMENTAL

Reagents

Vinyl formate (Monomer-Polymer, The Borden Co. Chemical Division)* was distilled through a 2-foot column filled with extruded stainless steel packing, and the fraction boiling at 46–47°C. was used.

Vinyl stearate (Air Reduction Chemical Co. and General Aniline and Film Co.) was recrystallized from acetone. The product exceeded the polymerization specification previously reported.⁷

All other chemicals used were either reagent grade or commercial materials and were used without further purification.

Polymerization Procedure

After a series of studies noting the effect of conditions of polymerization on the yield and on the solution viscosity properties, the following method was selected as a practical procedure. A solution of 200 g. vinyl formate, and vinyl stearate in varying molar proportions, 5.7 mole-% isopropanol, and 0.2–0.4 mole-% benzoyl peroxide (0.2 mole-% benzoyl peroxide was used for monomer mixtures containing 0–7.5 mole-% vinyl stearate, 0.3 mole-% for 8–15 mole-% vinyl stearate, and 0.4 mole-% for above 15 mole-% vinyl stearate) were sealed in a crown-capped bottle which had been thoroughly flushed with oxygen-free nitrogen, and the solution was heated at 30°C. for 24 hours with good agitation.

The crude copolymer was dissolved in a liter of acetone and was isolated by pouring its solution into 4 liters of methanol at room temperature and decanting the solvent. Residual monomer was removed from the copolymer mass by four extractions with 1 liter each of refluxing methanol for 3-hour periods. The copolymer was milled without heat as an aid in drying. The yields ranged from 70 to 90%, increasing with vinyl formate content.

Copolymer composition was computed from the saponification number for which the following procedure was used. A sample (of approximately half the equivalence of the saponifying reagent) was dissolved in 25 ml. pyridine and was treated with 25 ml. of 0.2 *N* aqueous KOH. The mixture was heated on the steam bath for 1 hour and the excess alkali was titrated with 0.1 *N* HCl to a phenolphthalein endpoint

$$\% \text{ vinyl formate} = \frac{\text{S.N.} - 180.7}{778.5 - 180.7} \times 100$$

* Mention of trade names or companies in this paper does not imply endorsement by the U. S. Department of Agriculture over others not mentioned.

where S.N. is the saponification number found for the sample whose composition was to be determined, and 778.5 and 180.7 are the saponification numbers of vinyl formate and vinyl stearate, respectively.

Hydrolysis Procedure

Several methods were used; the acid catalyzed aqueous heterogeneous hydrolysis was considered best.

(a) *Acid Catalyzed Aqueous Heterogeneous Hydrolysis*

The copolymer was suspended in water (10 ml./g.) at 95–97°C. and the mixture was treated with concentrated hydrochloric acid (2 ml./g.) and heated at 95–97°C. for 3 or 7 hours. The suspension was poured into 3 volumes of methanol, and the coagulated copolymer of vinyl alcohol and vinyl stearate was filtered off and dried at room temperature. (Copolymers containing 5 mole-% or more of vinyl stearate were isolated by decanting the aqueous phase and drying the crude copolymer.) It was then ground to a fine powder in a mechanical mill and extracted five times with 5 volumes of methanol per gram of copolymer to remove any stearic acid.

The purified copolymer was then analyzed by a differential saponification technique. The total alkali consumed in the saponification of a sample was first determined by the method previously given for copolymers of vinyl formate and vinyl stearate. A fresh sample was then taken; it was swollen by heating in 10 ml. of pyridine for 1.5 hours and was hydrolyzed with 15 ml. of approximately 0.5 *N* aqueous potassium hydroxide by refluxing until homogeneous (about 3–5 hours). While being cooled, the mixture was acidified by the dropwise addition of 6 ml. concentrated sulfuric acid and treated with 100 ml. methanol. From the resulting solution, methyl formate was slowly distilled into 50.00 ml. standard 0.1 *N* aqueous sodium hydroxide solution through a simplified Kjeldahl apparatus. The excess alkali was then back-titrated with 0.1 *N* HCl to a phenolphthalein endpoint. The composition of the copolymer was then calculated as follows: From the second titration

$$\% \text{ vinyl formate} = \frac{\text{meq. NaOH consumed} \times 72.06}{\text{mg. sample}} \times 100$$

From the data of the first titration and the value for the per cent vinyl formate:

$$\begin{aligned} \% \text{ vinyl stearate} &= \frac{\text{meq. NaOH consumed} \times 310.50 \times 100}{\text{mg. sample}} \\ &\quad - \% \text{ vinyl formate} \times \frac{310.50}{72.06} \end{aligned}$$

Per cent vinyl alcohol was then obtained by difference.

(b) Acid Methanolysis

The copolymer of vinyl formate and vinyl stearate was dissolved in ethylene chloride (15 ml./g. copolymer), then 0.15 ml. concentrated hydrochloric acid (0.01 ml./g.) was added, and methanol (7 ml./g.) was slowly stirred in. The solution was refluxed for 5 hours during which time the vinyl alcohol copolymer precipitated. It was filtered, washed with a liter of methanol, and dried.

(c) Emulsion Hydrolysis

A solution of the copolymer of vinyl formate and vinyl stearate in ethylene chloride (6 ml./g. copolymer) was stirred vigorously with 150 ml. of a 25% Triton W 30 solution (12 ml./g. containing 0.2% HCl) to effect emulsification. The emulsion was stirred and heated for 7 hours at 69–72°C. The polymer was recovered by pouring the emulsion into three times its volume of methanol at 20°C., filtering the residue, and drying.

Molecular Properties

Number- and weight-average molecular weights and constants derived from solution viscosity studies were used to describe the molecular characteristics of polymers and copolymers of vinyl formate. Acetone was used to prepare solutions of poly(vinyl formate), and tetrahydrofuran was used for those of the copolymers. All solutions were clarified by centrifugation followed by filtration through an ultrafine glass filter before being used. The concentration range was 0.5–2%. Viscosity measurements were made at 30°C. with an Ostwald type viscometer. A Fuoss-Mead osmometer with a denitrated nitrocellulose membrane was used for measuring the osmotic pressures from which the number-average molecular weights were determined. Weight-average molecular weights were determined from light-scattering measurements at 436 and 546 m μ for which a Brice-Phoenix⁸ photometer equipped with a cylindrical scattering cell⁹ was used.

Physical Properties

Direct molding of dried polymers and copolymers of vinyl alcohol was not possible because the samples decomposed and did not fuse properly. Sheets of poly(vinyl alcohol) or of copolymers of vinyl alcohol were prepared by swelling the powder with 33 parts of water for 24 hours and molding at 120°C. for 10 minutes at 1000 p.s.i. and cooling immediately to room temperature. Prior to test, the samples were stored at 23°C. and 50% r.h. to equilibrium (samples so treated are referred to as "equilibrated"), which was noted by attainment of weight constancy denoting absence of further loss of water. Other samples were dried at 100°C. for 3 days before being tested. Oriented samples were prepared by stretching the test strips from 2 to 6½ inches immediately after molding and keeping the samples under tension until equilibrium had been attained. The samples were then removed from the clamps and stored at 23°C. and 50% r.h. for 3 days before being tested.

The x-ray diffraction patterns of poly(vinyl alcohol) and its copolymers were determined with a GE-XRD-3 direct-recording unit using the following settings: slits, beam 3° ; detector 0.2° , soller MR; chart speed, 60 in./hr.; scanning speed, $2^\circ/\text{min.}$; linear scale, 2000; time constant, 2 sec.

The tensile strength and elongation at break were determined using an Instron tensile tester at a speed of 2 in./min. (When the per cent elongation at break exceeded 100%, a speed of 20 in./min. was used.) The brittle temperature was determined as the Clash and Berg¹⁰ T_f temperature.

Water uptake of copolymers of vinyl alcohol was measured by noting the increase in volume of a sample ($1 \times 1 \times 0.06$ in.) after being stored in water at 23°C. for 168 hours. The effect of water at 97°C. was noted qualitatively on the unformed sample.

RESULTS AND DISCUSSION

Establishment of Conditions for Polymerization of Vinyl Formate

It was necessary to determine practical conditions for the preparation of a grade of poly(vinyl formate) which on hydrolysis would give a poly(vinyl alcohol) having good mechanical properties. It was expected that the use of the same general procedure to prepare copolymers of vinyl alcohol and vinyl stearate would provide a copolymer having comparable structural properties and that, therefore, any differences in mechanical properties or in the effects of water would be attributable solely to the presence of the stearate groups.

The purity of the vinyl formate was the first consideration because the presence of acetaldehyde (a probable impurity) would undoubtedly have a serious effect on the molecular weight of the polymer. The intrinsic viscosity data in Table I show that the simple method for purifying vinyl formate given in the experimental section is satisfactory. Vansheidt and Chelpanova¹¹ polymerized a fraction of vinyl formate boiling in an $0.1\text{--}0.2^\circ\text{C.}$ range and obtained polymers (Table I, Experiments 1 and 2) which had intrinsic viscosities of 0.90 and 0.70. Because less carefully purified vinyl formate under comparable conditions gave intrinsic viscosities of 0.748 and 0.737 (Experiments 3 and 4), it was concluded that the method of purification of vinyl formate given above was adequate.

When a transfer agent was absent, however, the temperature of a large-scale mass polymerization could not be controlled and the resulting polymer was crosslinked. The addition of a small amount of isopropanol (Table I, Experiments 5 and 6) prevented gelation. The intrinsic viscosities of these resulting polymers may be compared (Table I, Experiments 7 and 8) with those prepared by the method of Hatchard and Hill⁶ who reported that a superior poly(vinyl alcohol) could be prepared therefrom. It will be noted that the intrinsic viscosities and k' values of the polymers of Experiments 5 and 6 are higher than those of 7 and 8. It was concluded, therefore, that the poly(vinyl alcohols) prepared by hydrolyzing the poly-

TABLE I
Effect of Method of Preparation on the Molecular Characteristics of Poly(vinyl formate)

Expt. No.	Solvent		Bz ₂ O ₂ , ^a mole-%	Temp., °C.	Yield, %	Viscosity props. ^b		Degree of polymerization Weight av.
	Type	Mole-%				[η]	Slope	Number av.
1 ^c	none		0.04	55	—	0.90	—	—
2 ^c	none		0.10	55	—	0.70	—	—
3	none		0.03	30	10	0.748	0.612	1.09
4	none		0.10	30	71	0.737	0.323	0.59
5	isopropanol	5.7	0.50	3	91	0.435	0.181	0.95
6	isopropanol	5.7	0.20	30	75	0.405	0.161	1.01
7 ^d	isopropanol	18	0.1 ^e	50	87	0.310	0.068	0.471
8 ^d	methanol	55	0.1 ^e	50	58	0.359	0.139	0.719
9	dioxane	5.7	0.3	30	82	0.420	0.171	0.97
10	dioxane	48	0.3	30	62	0.270	0.084	1.14
11 ^f	isopropanol	5.7	0.2	30	82	0.475	0.133	0.59
12 ^g	isopropanol	5.7	0.3	30	74	0.798	0.082	0.129
								3650
								1340
								4000
								4000
								3650
								3640
								2840

^a Benzoyl peroxide.

^b Huggins equation, ref. 16.

^c Data from Vansheidt and Chelapanova, ref. 11.

^d Approximate procedure of Hatchard and Hill, ref. 6.

^e Azobisisobutyronitrile.

^f Copolymer of vinyl formate containing 3 mole-% vinyl stearate.

^g Copolymer of vinyl formate containing 10 mole-% vinyl stearate.

mers of Experiments 5 and 6 would have approximately optimal mechanical properties and that the effect of vinyl stearate on the mechanical properties of the copolymers of vinyl alcohol prepared in the same manner could be validly appraised. A polymerization temperature of 30°C. was chosen when it was found that vinyl stearate is not completely soluble in the solution of isopropanol and vinyl formate given in the Experimental section at temperatures below 20°C.

The preparation of poly(vinyl formate) in methanol and dioxane were also investigated. The conditions of polymerization and the molecular characteristics of the resulting poly(vinyl formates) are given in Table I.

Copolymers of Vinyl Formate and Vinyl Stearate

Negligibly small differences were found between the compositions of the monomer mixtures and those of the resulting copolymers. Therefore, the assumption that the length of the acyl chain has no effect on the copolymerization reaction is valid. With increasing vinyl stearate content, the rate of copolymerization decreased and, therefore, higher initiator concentrations were used.

The molecular characteristics of two copolymers of vinyl formate containing 3 and 10 mole-% of vinyl stearate are given in Table I.

The physical properties of copolymers of vinyl formate and vinyl stearate resemble those of copolymers of vinyl acetate and vinyl stearate¹² in that the copolymers become softer and more flexible as the vinyl stearate content increases. For the same vinyl stearate content, however, the copolymers of vinyl formate are stiffer and harder than the vinyl acetate copolymers. In addition, they are less stable, hydrolyzing slowly.

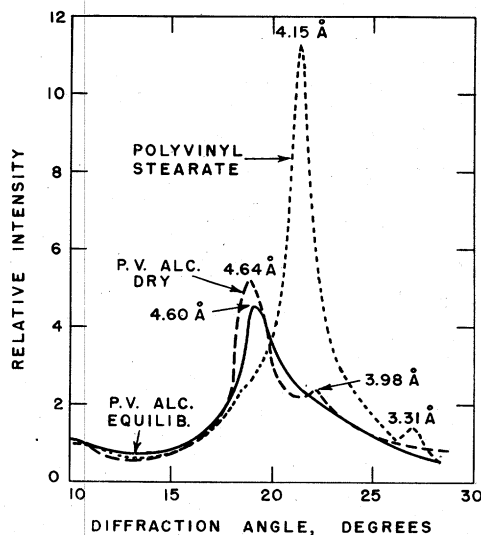


Fig. 1. X-ray diffraction patterns of dry and equilibrated polyvinyl alcohol and of polyvinyl stearate.

Investigation of the Structure of Copolymers of Vinyl Alcohol and Vinyl Stearate by X-Ray Diffraction

Figure 1 shows a portion of the x-ray diffraction patterns of equilibrated poly(vinyl alcohol) (containing about 8% of water), dried poly(vinyl alcohol), and poly(vinyl stearate). (The various recordings were adjusted to the same background level in the 10–16° range to make valid the comparison of the intensities measured.) In dry poly(vinyl alcohol), intense diffraction occurs at angles corresponding to spacings of 4.64 and 3.98 Å. It will be seen that when poly(vinyl alcohol) absorbs water, the peak corresponding to a spacing of 3.98 Å. disappears, the diffraction pattern becomes more diffuse, and the strongest diffraction maximum occurs at approximately 4.60 Å. compared with the sharper peak at 4.64 Å. noted in the dried poly(vinyl alcohol).

Poly(vinyl stearate) shows a very strong diffraction maximum at an angle corresponding to 4.15 Å., a weaker one at 3.31 Å., and one not shown in the figure which is due to a long spacing. These spacings are similar to those found¹³ for many long-chain aliphatic compounds. Hence, this suggests that the spacings observed for poly(vinyl stearate) are due to side-chain crystallization.

The maxima associated with both poly(vinyl alcohol) (4.64 Å.) and poly(vinyl stearate) (4.15 Å.) appear in the x-ray diffraction patterns of copolymers containing more than about 5 mole-% vinyl stearate. The diffraction due to the vinyl stearate increases roughly proportionately with its content. Figure 2 shows the change in the diffraction pattern of poly(vinyl alcohol) caused by 5.84 mole-% of vinyl stearate. It will be observed that the 4.64 Å. maximum of dry poly(vinyl alcohol) has become more diffuse and that the 3.98 Å. maximum appears only as a shoulder. No distinct peak in the vicinity of the 4.15 Å. maximum observed for poly(vinyl stearate) can be distinguished. However, in the equilibrated sample (i.e., containing about 8% water) a maximum at 4.21 Å., possibly attributable to a structure similar to that which gives rise to the 4.15 Å. spacing in poly(vinyl stearate), can be observed. If, at a very rough approximation, the scattering in this region due to the wes

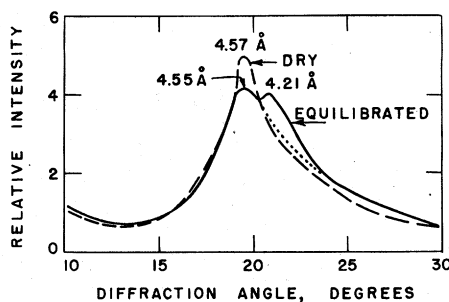


Fig. 2. X-ray diffraction patterns of dry and equilibrated copolymers of vinyl alcohol containing 5.84 mole-% vinyl stearate.

poly(vinyl alcohol) alone is indicated by the dotted line normalizing the 4.55 Å. peak, the observed scattering increment above this line is the poly(vinyl stearate) contribution. It will be noted that the intensity increment is roughly 5% of the 4.15 Å. maximum. This suggests that, to some extent, in the equilibrated sample the two monomer units are crystallizing, each in its own lattice.

In Figure 3 the effect of a larger amount (15.8 mole-%) of vinyl stearate on the lattice of poly(vinyl alcohol) is shown. The maximum for the dry sample is reduced in intensity and is shifted to an angle corresponding to a spacing of 4.44 Å. (from 4.64 Å.); the entire pattern is more diffuse. No diffraction associated with poly(vinyl stearate) can be distinguished. In the equilibrated sample, the most notable feature is the sharp peak resembling that related to the 4.15 Å. spacing in poly(vinyl stearate). After being held at room temperature for 2 months, the equilibrated sample was re-examined by means of its x-ray diffraction pattern. Surprisingly, it

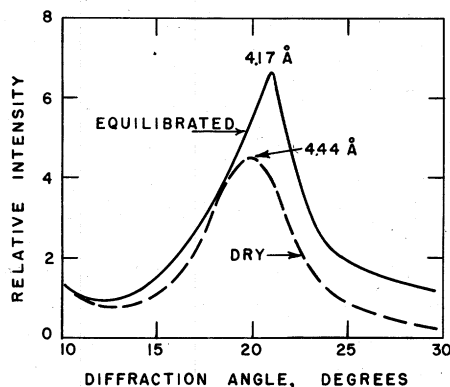


Fig. 3. X-ray diffraction patterns of dry and equilibrated copolymers of vinyl alcohol containing 15.82 mole-% vinyl stearate.

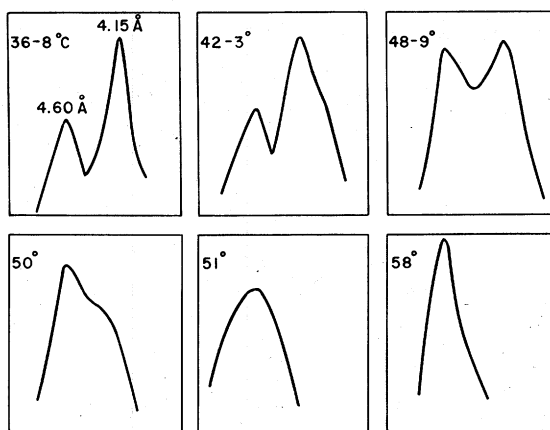


Fig. 4. Effect of temperature on the x-ray diffraction pattern of a copolymer of vinyl alcohol containing 15.82 mole-% vinyl stearate. Melting-out of stearate crystallites.

was found that a poly(vinyl alcohol) peak had developed similar to the one shown in the first curve in Figure 4. This suggested that the vinyl stearate segments and the vinyl alcohol segments formed separate phases. If this were indeed the case, then it should be possible to melt out the lower melting phase while not affecting, or perhaps even enhancing, the second phase. Because poly(vinyl stearate) melts sharply at about 50°C. whereas poly(vinyl alcohol) decomposes well above 100°C., the differential melting should be observable experimentally. This is shown in Figure 4 where smoothed-out portions of the x-ray diffraction pattern taken at various temperatures are reproduced. The temperature was increased slowly—at the rate of about 1°C./min.—to permit crystalline changes to occur. At 42–43°C., which is just below the melting range of poly(vinyl stearate), the stearate peak became more diffuse. As melting occurred at 48–49°C., the two peaks began to merge because they were so diffuse, but the alcohol peak had increased in intensity suggesting that it had grown at the expense of the stearate. At 50°C., the stearate peak had practically disappeared and was visible only as a shoulder and because it created a diffuse pattern. At 51°C., the effect of the stearate crystallinity was scarcely visible as a diffuse pattern and at 58°C., a sharp, intensified poly(vinyl alcohol) peak only was observed.

The observations on the diffraction pattern of the copolymers lead to the following conclusions.

1. In copolymers of vinyl alcohol and vinyl stearate, two distinct lattices are probably present. One, apparently, is due to the separate crystallization of the alcohol portion of the copolymer, the other to the stearate portion of the copolymer. If this were not the case, if in a copolymer the stearate and alcohol groups had crystallized together, a completely new lattice should have been observed with distinctly different diffraction maxima instead of the observed small shifts from the peaks in the homopolymers.

2. In the dry state, the poly(vinyl alcohol) lattice is the predominating factor and has a retarding effect on the formation of crystallites by the vinyl stearate units.

3. When the poly(vinyl alcohol) lattice is weakened by the presence of the water of equilibration, the vinyl stearate units are free and are able to crystallize in a lattice resembling poly(vinyl stearate).

Physical Properties

Solubility. The effect of the stearate content on the resistance of the copolymers of vinyl alcohol to water absorption at 23°C. is shown in Table II. As little as 1.46 mole-% has a pronounced effect. At 98°C., poly(vinyl alcohol) (whether oriented or not) completely dissolves in water in a few minutes whereas, after 2½ hours, copolymers containing as little as 1.46 mole-% of vinyl stearate are insoluble although swollen. The criterion of insolubility was failure to produce cloudiness when the water in which the copolymers had been heated was poured into an excess of methanol. The

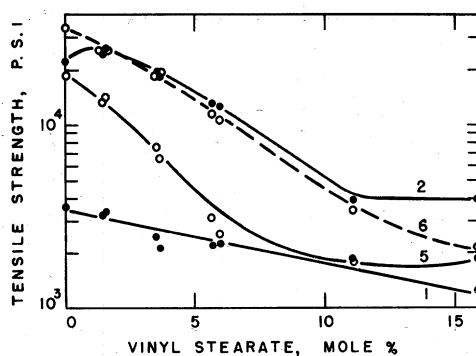


Fig. 5. Effect of stearate content and drying on the tensile strength of copolymers of vinyl alcohol. Curve 1, equilibrated unoriented; Curve 2, equilibrated, oriented; Curve 5, dried, unoriented; Curve 6, dried, oriented.

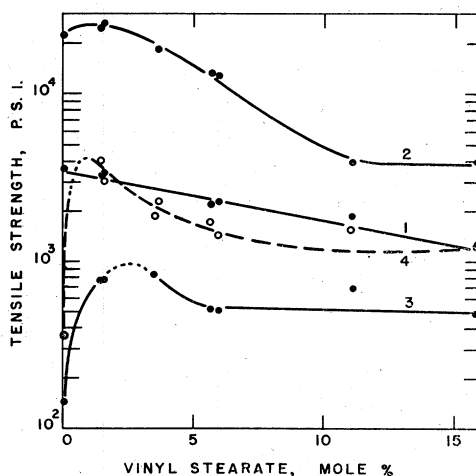


Fig. 6. Effect of water treatment on the tensile strength of copolymers of vinyl alcohol. Curve 1, equilibrated, unoriented; Curve 2, equilibrated, oriented; Curve 3, unoriented, stored in water; Curve 4, oriented, stored in water.

copolymers are not crosslinked because they are soluble in various mixtures of pyridine and water. For example, a solution of 7 volumes of pyridine and 2 volumes of water will dissolve copolymers containing 0–5 mole-% of vinyl stearate.

Tensile Properties. It was noted, previously, that as the fatty monomer content in copolymers of vinyl chloride and vinyl stearate,¹⁴ or of vinylidene chloride and octadecyl acrylate¹⁵ increased the tensile strength decreased. A similar effect was noted among copolymers of vinyl alcohol and vinyl stearate with important modifying effects of water and of orientation being present also. Thus, Figure 5, Curve 1 shows that increasing the vinyl stearate content in equilibrated vinyl alcohol copolymers decreases the tensile strength. When these samples are oriented (Curve 2), the tensile strengths of all the samples are increased, but the tensile strength again

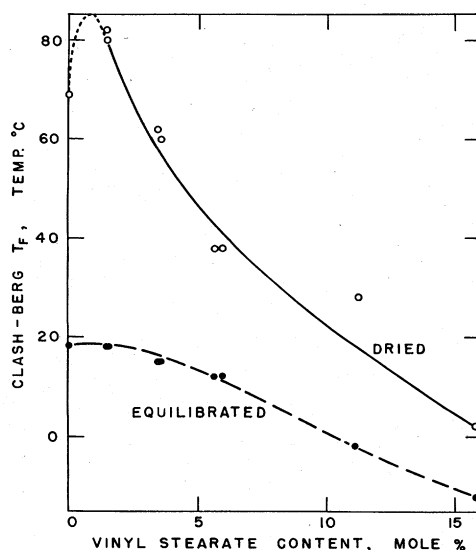


Fig. 7. Variation of brittle temperature of copolymers of vinyl alcohol with vinyl stearate and water content.

decreases as the vinyl stearate content increases. When the unoriented samples, whose properties are shown in Curve 1, were dried for 3 days at 100°C. their tensile strengths increased, as shown in Curve 5. Drying oriented samples, however, did not materially alter their tensile strengths (Curve 6).

The effect on their tensile strengths of immersing samples of equilibrated unoriented and oriented copolymers in water at 23°C. for 8 days is shown in Figure 6. (Curves 1 and 2 are reproduced from Figure 5 for comparison.) Curve 3 is drawn from data for unoriented samples and Curve 4 for oriented samples. Although the tensile strength of all the samples was decreased by immersion in water, poly(vinyl alcohol) suffered the greatest loss. The tensile strength of unoriented poly(vinyl alcohol) dropped to about 5% and the oriented sample to about 1% of their respective original strengths. As Curves 3 and 4 show, a significantly smaller change in tensile strength on immersion was noted for the copolymer samples. Thus, it may be concluded that the vinyl stearate segments partially prevent the destruction of the poly(vinyl alcohol) lattice structure.

The vinyl stearate content did not affect the elongation at break (which ranged from 3 to 17%) in the dried vinyl alcohol copolymer samples. In the equilibrated samples, the per cent elongation decreased sharply from 330 to 5% as the vinyl stearate content increased from 0 to 15.8 mole-%.

Brittle Temperature. The effect of the vinyl stearate content and of water on the brittle temperature is shown in Figure 7. An inverse relationship between the vinyl stearate content and the brittle temperature is evident. Similar effects were observed in other instances of internally plasticized polymers.

The water retained during equilibration of the test samples further plasticized the copolymers. It had a greater effect at the low stearate concentrations.

TABLE II
Absorption of Water by Vinyl Alcohol Copolymers^a

Vinyl stearate content, mole-%	Volume increase, %	
	Unoriented	Oriented
0	219	165
1.46	95	58
3.61	81	55
5.66	66	55
15.82	12	10

^a Sample immersed in water at 23°C. for 8 days.

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Synopsis

Copolymers of vinyl formate containing various amounts of vinyl stearate were prepared by mass polymerization at 30°C. in the presence of small amounts of isopropanol. A study of the molecular weights and the viscosity properties of these copolymers indicated that they have high degrees of polymerization and are little branched. A study of the x-ray diffraction patterns of the copolymers of vinyl alcohol and vinyl stearate indicated that the alcohol and stearate segments crystallize in separate lattices. The tensile strength of vinyl alcohol copolymers decreased as the vinyl stearate content increased

and as their water content increased. When the samples were dried or were oriented, their tensile strengths increased. Copolymers of vinyl alcohol containing as little as 1.5 mole-% of vinyl stearate had greatly improved resistance to water and were insoluble in water at 98°C.

Résumé

Les copolymères du formiate de vinyle contenant des quantités variables de stéarate de vinyle ont été préparés par polymérisation en block à 30°C en présence de faibles quantités d'isopropanol. Une étude des poids moléculaires et des propriétés viscosimétriques de ces copolymères indiquent qu'ils ont des degrés de polymérisation élevés et sont peu ramifiés. Une étude des réseaux de diffraction aux rayons-X des copolymères d'alcool vinylique et de stéarate de vinyle indique que les segments alcooliques et stéariques cristallisent en des réseaux séparés. La résistance à la traction des copolymères d'alcool vinylique décroît avec une augmentation de la teneur en stéarate de vinyle et de leur teneur en eau. Lorsque les échantillons étaient séchés ou soumis à orientation, leurs résistances à la traction s'améliorent. Les copolymères d'alcool vinylique contenant aussi peu que 1.5 mole-% de stéarate de vinyle ont une résistance à l'eau considérablement améliorée, et sont insolubles dans l'eau à 98°C.

Zusammenfassung

Copolymere von Vinylformat, die verschiedene Mengen an Vinylstearat enthalten, wurden durch Massenpolymerisation bei 30°C in Gegenwart von kleinen Mengen von Isopropanol hergestellt. Eine Untersuchung der Molekulargewichte und der Viskositätseigenschaften dieser Copolymere zeigte an, dass sie hohe Polymerisationsgrade haben und wenig verzweigt sind. Eine Untersuchung der Röntgenstrahlen-Diffraktionsdiagramme der Copolymere von Vinylalkohol und Vinylstearat zeigte an, dass die Alkohol- und Stearatsegmente in verschiedenen Netzwerken kristallisieren. Die Reißfestigkeit der Vinylalkohol-Copolymere nahm mit Zunahme des Vinylstearatgehaltes und Zunahme ihres Wassergehaltes ab. Wenn die Proben getrocknet oder orientiert wurden, nahm ihre Reißfestigkeit zu. Copolymere von Vinylalkohol, die nur 1,5 Mol% Vinylstearat enthielten, hatten eine stark verbesserte Widerstandsfähigkeit gegen Wasser und waren in Wasser bei 98°C. unlöslich.

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